Thermal Degradation of Polymers. XXII. Vacuum Pyrolysis of Poly(*m*-N,N-dimethylaminostyrene); the Residue and the Fraction Volatile at Pyrolysis Temperature, Involatile at Room Temperature

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Synopsis

The effect of extent of degradation of poly(*m*-N,N-dimethylaminostyrene) on the quantity and molecular weight of the residue is described. Comparative studies on polystyrene and poly(*m*-N,N-dimethylaminostyrene) have indicated significant differences between the two polymers. Torsional braid analysis has shown the crosslinked residue from poly(*m*-N,N-dimethylaminostyrene), produced at temperatures greater than 150°C, to be obtained on the heating cycle rather than the cooling cycle, and mechanisms to account for this phenomenon are discussed. The physical form of the residue has been found to be molecular weight dependent, and this has been discussed in terms of the differences in "melt temperature" relative to the "onset temperature" for crosslinking. The quantity and composition of the fraction volatile at pyrolysis temperature, involatile at ambient temperature are discussed. The components of this fraction were identified by GPC and mass spectrometry and include oligomers containing the secondary amino function. Mechanisms involving N-alkyl and N-aryl scission are proposed to account for the observed products.

INTRODUCTION

In a previous paper[1] we reported the effect of temperature and polymer molecular weight on the products of degradation of poly(*m*-N,N-dimethylaminostyrene) (P*m*DAS) volatile at pyrolysis and at ambient temperature under high vacuum. Polystyrene (PS) degradation was similarly monitored under identical conditions for comparative purposes. Three major differences were observed for these fractions.

a. The liquid fraction from P*m*DAS contained a greater number of components than that from PS and included secondary amines and aromatic hydrocarbons.

b. The monomer yield from P*m*DAS was significantly lower than that from PS and molecular weight dependent.

c. The N,N-dimethyl-substituted component corresponding to toluene in PS degradation was present in increased quantity in the P*m*DAS liquid fraction and was molecular weight dependent. Mechanisms involving methyl group migration to chain radicals, thereby reducing the "zip length," have been proposed to account for the reduced monomer yield. The complexity of the products from P*m*DAS has been ascribed to N-alkyl and N-aryl bond scission and the subsequent reactions of the generated radicals. The molecular weight dependence of the system has been discussed in terms of the differences in physical form of the polymers as a result of heating.

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We now report studies on (a) the fraction volatile at pyrolysis temperature and involatile at ambient temperature and (b) the residue.

EXPERIMENTAL

Materials

The materials were as previously described.[1]

Apparatus and Procedure

Nuclear magnetic resonance (NMR) and gas–liquid chromatography (GLC) were carried out as previously described in part XXI.[1]

Infrared spectra were recorded as previously for soluble components. P*m*DAS, which yielded partially soluble or insoluble residues on pyrolysis, was cast on rock-salt plates from toluene or chloroform with subsequent pyrolysis of these thin films.

Torsional Braid Analysis (TBA)

TBA was employed to study the change in relative rigidity of polymer samples with temperature in the range ambient to 225°C. A braid of glass fibers ("E" glass rovings ex TBA Ltd., 2 rovings/braid, 816 strands/roving, 8.5 cm length), previously heated to 500°C in a muffle furnace for 1 hr, was soaked in 30% (w/v) solution of polymer to impregnate the braid. The braid was allowed to air dry and then treated in an air-circulating oven for 1 hr at a temperature 5–10°C above the T_g. The braid was then suspended in a similar apparatus[3] to that described by Gillham and co-workers.[4,5] A nitrogen flow rate of 60 ml/min was employed through the apparatus which was heated at 3°C/min (nominal).

Vacuum Pyrolysis

Studies were carried out in the apparatus previously described.[1,2] Pyrolysis was effected as before in a Pyrex glass tube sample container closed at one end, and the two fractions were obtained as described below.

Fraction III—The Residue

Samples of PS and P*m*DAS were pyrolysed for 45 min at temperatures between 150 and 400°C. The residues obtained in the glass tube were used for GPC studies by the method reported previously.[1] PS residues remained soluble at all pyrolysis temperatures, whereas P*m*DAS became insoluble, yielding a gel.

The residues from P*m*DAS were shaken at ambient in tetrahydrofuran (THF) for 12 hr, and the sol fraction was obtained by filtration.

Fraction IV—The Oil Fraction

This was obtained from P*m*DAS after pyrolysis at temperatures between 350 and 500°C as a viscous oil in the pyrolysis tube. A general pyrolysis time of 45 min was again used and 4 hr allowed for the system to come to equilibrium, as
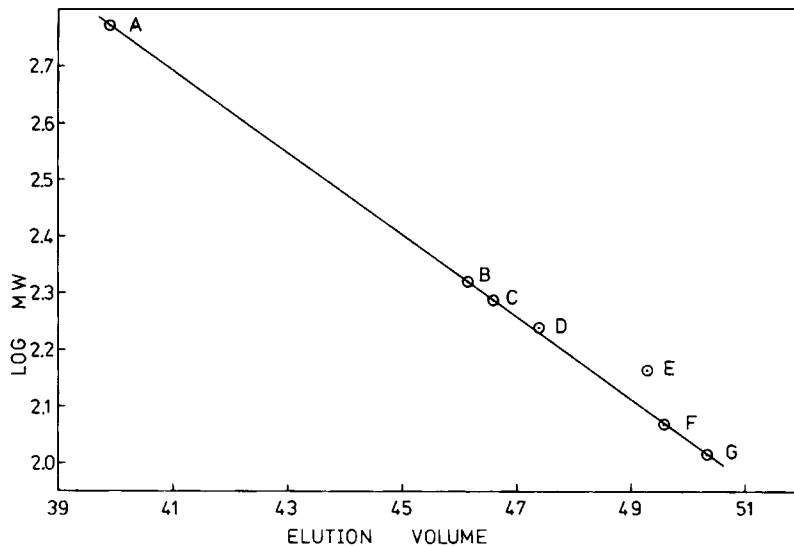
Fig. 1. GPC calibration curve: (A) PS 600; (B) 2,4-diphenylbutane; (C) 1,3-diphenylpropane; (D) p-N,N-diethylaminostyrene; (E) m-N,N-dimethylaminostyrene; (F) α-methylstyrene; (G) styrene.

described in part XXI.[1] The oil fractions from PS and PmDAS were extracted from the pyrolysis tube as described in part XXI.[1] The oil fractions from PS and PmDAS (after equilibriation) were subjected to GLC analysis for monomer, which was shown to be absent. The oil was qualitatively analyzed by IR and NMR and by MS using an AEI MS902 fitted with a direct probe. Probe temperatures between ambient and 300°C were employed. MS/GLC studies were performed using a short glass column (46.5 cm × 4 mm) containing 15% SE30 on Chromosorb W,AW-DMCS (80–100 mesh) maintained at 100°C which was programmed to 250°C at 20°C/min on injection of a 5-μl sample. A molecular separator was used to remove the helium carrier gas from the eluted components before they were introduced into the ionization chamber of the MS 902 mass spectrometer.

Gel permeation chromatography (GPC) was effected on the oil fraction as a 0.5% (w/v) solution in THF. This solution was injected into five columns containing crosslinked PS beads with pore size distributions 700–2000, 200–500, 150–350, 100, and 50–80 Å. A double detector system which allowed the simultaneous recording of ΔRI and ΔUV with elution volume was employed.

TABLE I
Appearance and Solubility Characteristics of PS and PmDAS Residues

Source of residue[a]	Appearance	Solubility characteristics
PS 6 and 7	clear colorless glass	soluble in toluene and chloroform
PmDAS 1 and 2	clear yellow-brown glass	insoluble with gel formation
PmDAS 4 and 5	remains as an opaque fibrous material up to 100% volatilization, color changed from very pale yellow to dark brown	insoluble with gel formation

[a] See ref. 1.

TABLE II
Weight Loss and Solubility Studies on PmDAS Residues[a]

Sample		150°C[b]	200°C	250°C	350°C
PmDAS 4	Solubility	I	I	I	I
	Percent weight loss	0.1	0.1	0.9	64.0
PmDAS 3	Solubility	Is	I	I	I
	Percent weight loss	0.5	0.5	1.5	44.6

[a] I = Insoluble in toluene; Is = mainly soluble with slight amount of gel formation.
[b] Pyrolysis temperature.

The system was calibrated using PS 600 and a series of "styrene" standards and monomers of aminostyrene polymers. Peak maxima were used to determine the point of elution for all standards. A plot of the log of molecular weight against elution volume gave the relationship shown in Figure 1.

RESULTS AND DISCUSSION

Fraction III—The Residue

The appearance and solubility characteristics of the residues obtained after pyrolysis of PS and PmDAS samples of different molecular weights in the temperature range of 350–400°C are summarized in Table I. The data presented in the table again highlight the molecular weight dependence of the PmDAS
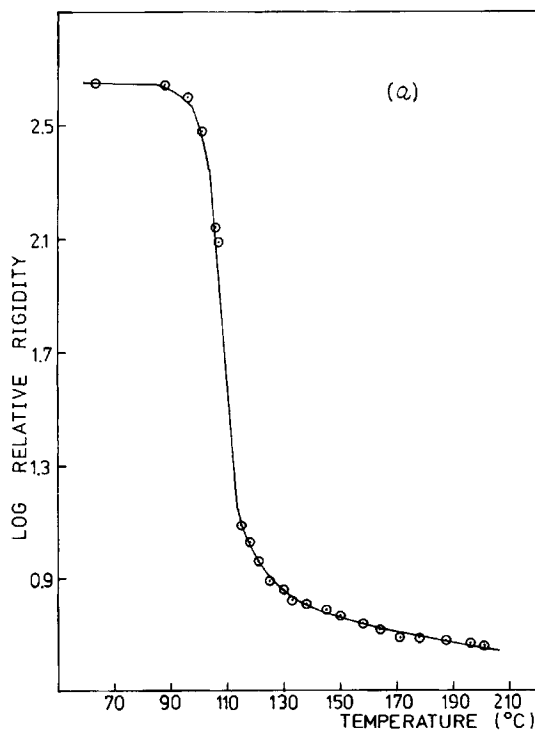
Fig. 2. (a) Torsional braid analysis of PS; (b) torsional braid analysis of PmDAS 2; (c) torsional braid analysis of PmDAS 4; (——⊙——) heating cycle; (——△——) cooling cycle.
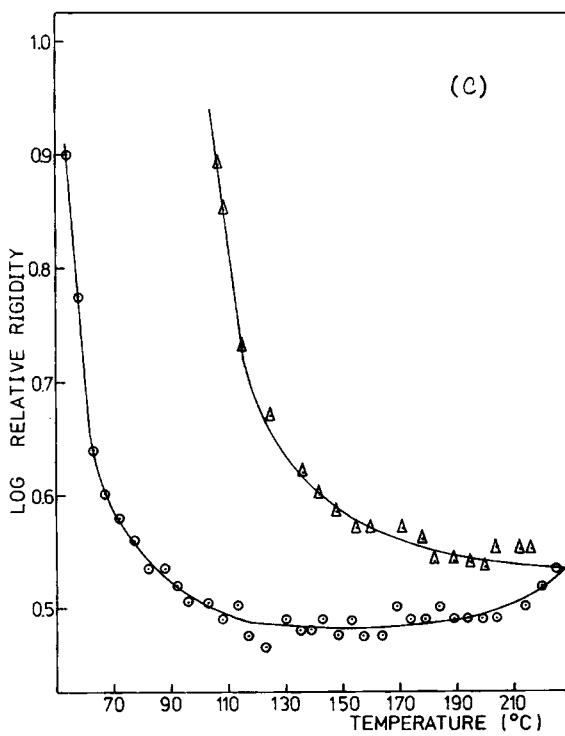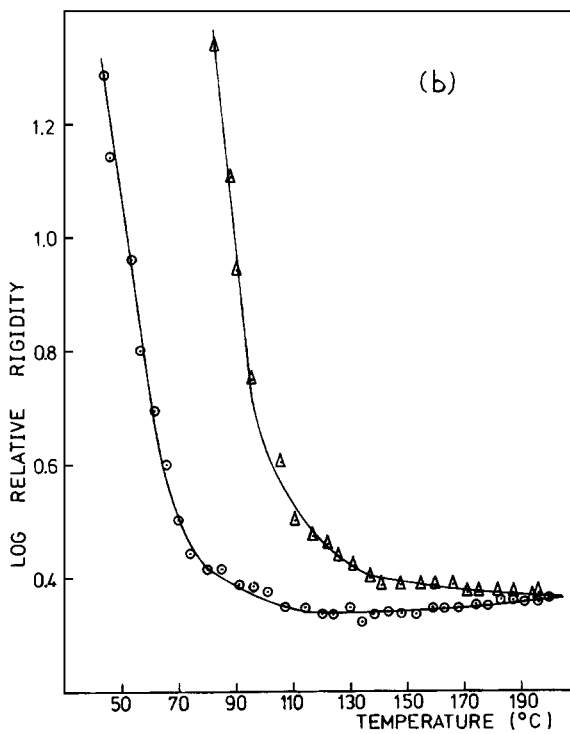
Fig. 2. *(Continued from previous page.)*

system. Studies on the isomeric poly(p-N,N-dimethylaminostyrene) (PDAS) indicated that crosslinking also occurred but that this material gave colored glasses in the molecular weight range studied.[6] IR spectra recorded on PS and PmDAS residues obtained from pyrolyses at temperatures up to 400°C failed to reveal any significant differences from those of the untreated polymer. Combustion analysis of PmDAS 4 similarly gave no significant change from the untreated polymer.

In attempting to establish the temperature at which PmDAS became insoluble and if insolubility was related to volatile formation, a series of pyrolyses were carried out at temperatures below 350°C. The results from these studies are summarized in Table II. The results shown in the table suggest that the onset of insolubility is accompanied by volatile evolution as suggested by the slight pressure increase observed on the pyrolysis rig at these temperatures. When the polymer was heated to 200°C after first degassing the system at a temperature 10°C above the T_g, the products were monitored using the MS in its high-resolution mode. Ions at m/e 16 (CH_4^+) and 15 (CH_3^+) and low intensity ions at m/e 30 ($C_2H_6^+$) and 29 ($C_2H_5^+$), indicating presence of methane and ethane, were observed which increased in prominence between 200 and 220°C.

The temperature at which a crosslinked residue was obtained for PmDAS was significantly lower than that observed for PDAS. On reheating to 360°C the residue from PDAS was found to give a similar monomer yield to that from the untreated polymer. This led Still and Whitehead[6] to suggest that insolubility was associated with thermolabile C–N or N–N crosslinks formed on cooling of the residue, and they argued that these links would break preferentially on reheating and therefore would not inhibit degradative processes.

Studies were made on PS and PmDAS by TBA in an attempt to establish whether crosslinking occurred during the heating or cooling cycle. Stadniki and coworkers[7] have shown that for PS the relative rigidity decreases sharply at the T_g and then continues to decrease slowly up to 200°C. On cooling the relative rigidity was found to retreat along the same curve. The results obtained in this study are shown in Figures 2(a) to 2(c) and those for PS are similar to those found
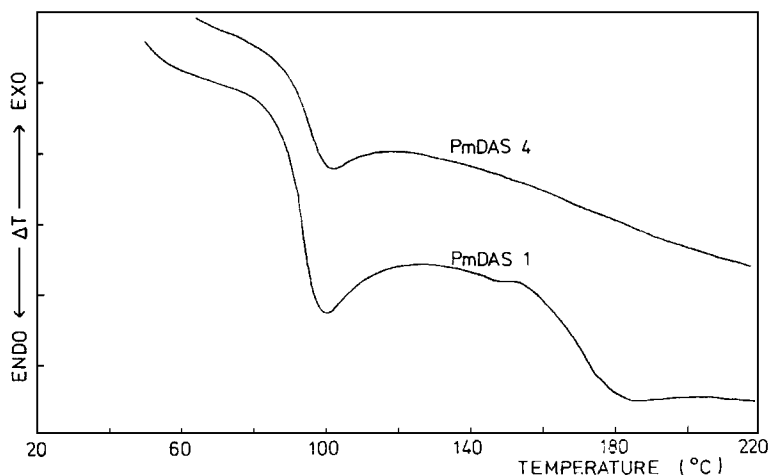

Fig. 3. DSC curves for PmDAS 1 and PmDAS 4. Heating rate, 30°C/min; sensitivity, ΔT = 0.2°C/in., sample weight PmDAS 1, 19 mg; PmDAS 4, 11 mg; atmosphere, static nitrogen.
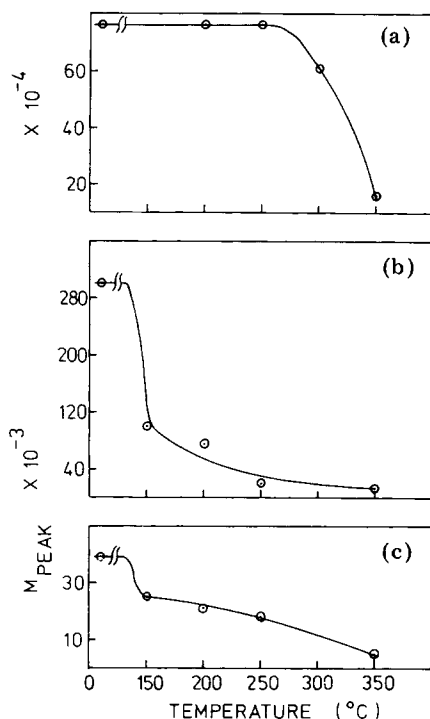
Fig. 4. Effect of degradation temperature on molecular weight: (a) PS; (b) PmDAS 4; (c) PmDAS 3.

TABLE III
Analysis of PS and PmDAS Oligomer Fractions by GPC

Source of fraction IV	Peak no.	Molecular weight at peak maximum	Assignment
	1	211	dimers
PS	2	319	trimers
	3	421	tetramers
	4	506	pentamers
	1	288	dimers
PmDAS	2	451	trimers
	3	602	tetramers

by Stadniki.   Those obtained for PmDAS 2 and 4 show an increase in rigidity with increasing temperature above the T_g which is particularly dominant in PmDAS 4 at 200–210°C.   This suggests that crosslinks are formed during the heating cycle but does not preclude formation of thermolabile crosslinks on cooling.

The T_g values observed on the heating and cooling cycles for PmDAS are different, and while this may in part be due to crosslinking, the T_g on the heating cycle is likely to be depressed by retained solvent.

In Table I it was reported that PmDAS 4 remained as an opaque fibrous material throughout the course of degradation, whereas PmDAS 2, the lower mo-

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TABLE IV
Components Present in PS and PmDAS Oligomer Fraction Identified by Their Molecular Ions[a]

PS m/e	PmDAS m/e	Assignment
196	282	H₃C—CH₂—CH₂ with X substituents
208	294	H₂C=C—CH₂—CH₂ with X substituents
220	306	H₂C=C—CH₂—C=CH₂ with X substituents
312	441	H₂C=C—CH₂—CH—CH₂—CH with X substituents
416	—	H₂C=C—CH₂—CH—CH₂—CH—CH₂—CH with X substituents
194	280	H₃C—CH=CH with X substituents
298	427	H₃C—CH—CH—CH=CH with X substituents
402	—	H₃C—CH—CH—CH—CH—CH=CH with X substituents

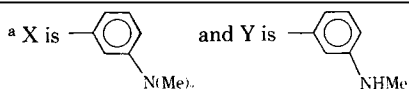[a] X in PS is —C₆H₅ (phenyl) and X in PmDAS is —C₆H₄—N(Me)₂

lecular weight sample, collapsed into a "melt phase" and yielded clear, glassy residues on cooling. This behavior was confirmed by hot-stage microscopy under nitrogen when the low molecular weight sample was seen to collapse into a "molten" film at 135–140°C whereas, although the high molecular weight sample collapsed slightly at the T_g, it remained fibrous to 300°C. Similar observations were made when samples of PmDAS were presented to a hot stage maintained at 240°C; the low molecular weight sample gave a melt after ≃3 sec while the high molecular weight fibrous sample remained unchanged. The difference in physical appearance of residues from PmDAS may possibly be explained in terms of crosslinking in relation to the flow temperature.

The physical significance of the flow temperature in PS, attributed to the T_{LL} transition (liquid–liquid transition temperature) by Stadniki and co-workers,[7] is the point at which changes in the state of localized order and the onset of motion of entire polymer chains occurs. The higher the molecular weight then the more difficult it is to displace the molecule as a whole and the higher the flow temperature or T_{LL}. In the case of PS, Stadniki and co-workers[7] have shown by DSC studies that the T_{LL} for PS of $\overline{M}_n$ 23,500 is 157°C and that for PS of $\overline{M}_n$ 111,000 is 190°C.

In PmDAS, where crosslinking has been shown to occur at relatively low temperatures, the low molecular weight polymer will probably have passed

TABLE V
Components Present in Fraction IV from PmDAS Containing Secondary Amino Groupings[a]

| m/e	Assignment
268	H₂C—CH₂—CH₂ with X, Y substituents
254	H₂C—CH₂—CH₂ with Y, Y substituents
280	H₂C=C—CH₂—CH₂ with X, Y substituents
266	H₂C=C—CH₂—CH₂ with Y, Y substituents
427	HC=C—CH₂—CH—CH₂—CH₂ with X, Y, X substituents
266	H₂C—CH=CH with X, Y substituents
413	H₂C—CH₂—CH—CH=CH with X, Y, X substituents
252	H₂C—CH=CH with Y, Y substituents

[a] X is —C₆H₄—N(Me)₂ and Y is —C₆H₄—NHMe

through the T_{LL} transition and formed a "melt" prior to crosslinking. In the high molecular weight polymer the T_{LL} may be greater than the temperature at which crosslinking begins, resulting in maintenance of "fiber" structure. Hot stage microscopy, as discussed, supports this conclusion. DSC studies were also made under the conditions reported by Stadniki[7] in order to determine the T_{LL} transition for high and low molecular weight samples of PmDAS.

The results obtained are shown in Figure 3. PmDAS 1 gave a T_{LL} whereas PmDAS 4 gave no indication of T_{LL} up to 210°C. While the nature of the T_{LL} transition is the subject of controversy, these studies demonstrate that the low molecular weight polymer forms a "melt" just before, or approximating to, the temperature at which a crosslinked residue was obtained. The high molecular weight polymer has a T_{LL} or flow temperature in excess of the temperature at which crosslinking begins.

Comparative studies have been made on the effect of degradation temperature on the molecular weight of PS and PmDAS samples 3 and 4, and these are presented in Figure 4. PS showed a molecular weight decrease at approximately 250°C in accord with data reported by Jellinek[8] and Grassie and Kerr.[9] The sol fractions from PmDAS samples suggest that a molecular weight decrease occurs at the same temperature as the onset temperature for crosslinking (≃150°C). If this molecular weight decrease was due solely to the insolubility

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TABLE VI
Further Components Present in Fraction IV from PmDAS

| m/e	Assignment
296	H₃C—CH₂—CH—R ; with X below CH₂ and CH
308	H₂C=C—CH₂—CH—R ; with X below C and CH
453	HC=C—CH₂—CH—CH₂—CH—R ; with X below C, CH, CH
251	HC=CH—CH₂ ; with Z below, X below
253	H₃C—CH₂—CH₂ ; with Z below, X below
265	H₃C=C—CH₂—CH₂ ; with X below, Z below
412	HC=C—CH₂—CH—CH₂—CH₂ ; with X, Z, X below
237	HC=CH—CH₂ ; with Z′ below, X below
239	H₃C—CH₂—CH₂ ; with Z′ below, X below
251	HC=C—CH₂—CH₂ ; with Z′ below, X below

a R is CH₃, X is —⟨◯⟩N(Me)₂ , Z is —⟨◯⟩CH₃ , and Z′ is —⟨◯⟩H

of high molecular weight species because of molecular entanglement in a cross-linked network, then the decrease in molecular weight should be accompanied by a change in the breadth of the molecular weight distribution without affecting its overall position.

In practice a change in distribution is observed which results in the distribution being shifted to lower molecular weights. This suggests that chain scission at low temperature is responsible for some of the observed molecular weight decrease. In PS the observed drop has been ascribed to weak links formed during polymerization.[8,9] Again such links could be present in the PmDAS system. Crosslinking in PmDAS may occur via a similar mechanism to that proposed for PDAS by Still and Whitehead,[6] namely, N-alkyl cleavage to give alkarylamino radicals which may combine to give crosslinks. However, in such systems other

reactions are also possible for the alkarylamino radical and the methyl radical which are formed. Thus a molecular weight decrease can occur by inter- or intramolecular transfer reactions that lead to chain scission:

$$Y\bullet \;+\; {-}CH_2{-}\underset{\underset{X}{|}}{CH}{-}CH_2{-}\underset{\underset{X}{|}}{CH}{-}$$

$$\downarrow$$

$$YH \;+\; {-}CH_2{-}\underset{\underset{X}{|}}{\overset{\bullet}{C}}{-}CH_2{-}\underset{\underset{X}{|}}{CH}{-}$$

$$\downarrow$$

$${-}CH_2{-}C{=}CH_2 \;+\; \bullet\underset{\underset{X}{|}}{CH}{-}$$

where X is (phenyl)${-}N(Me)_2$ and Y is $CH_3\bullet$ or (phenyl)${-}\overset{\bullet}{N}Me$
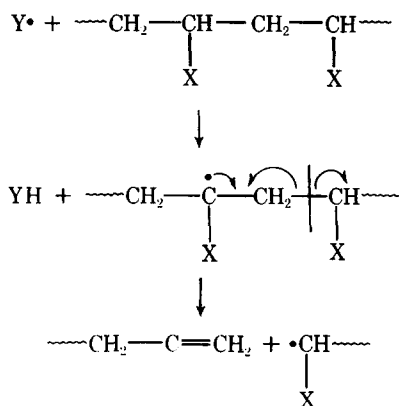
attached to the same or a different chain.

Evidence for alkarylamino radicals and methyl radicals has previously been given from MS analysis of the volatile products produced on crosslinking and from studies of the liquid fraction, part XXI.[1] The coloration similarly may result from trapped radicals since trapped radicals were shown to be present in previous studies on poly(*m*-aminostyrene) (PAS) and PDAS.[6,10]

The formation of thermolabile crosslinks was proposed to explain the behavior of PDAS.[6] In addition to combination, alkarylamino radicals may also disproportionate in the manner described for the methylphenylamino radical,[11] namely,

$$2\,Ph - \overset{\bullet}{N} - Me \rightarrow PhNHMe + H_2C{=}NPh$$
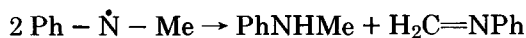
Such reactions in the case of P*m*DAS would lead to structures of the type

(structure) and (structure)
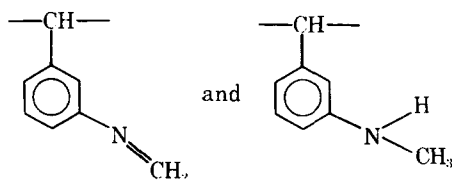
which could form a crosslink with a polymer chain radical or an alkarylamino radical (R•):

(structure) + R• → (structure)
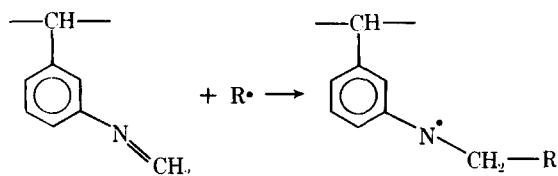
There also exists the possibility of radical substitution into an activated aromatic nucleus which could occur inter- or intramolecularly. Aromatic substitution by phenyl radicals is well known,[12] but the reactions of alkarylamino radicals have only briefly been studied.[11,13] In PS it is apparent that chain end radicals do not undergo ready substitution in the aromatic rings since a crosslinked system is not obtained.

In the analysis of liquid fraction (part XXI), evidence was presented to show that N-aryl cleavage also occurred, giving rise to substituted phenyl radicals also capable of forming crosslinks.

While it is easy to speculate on the nature of the crosslinks, it is much more difficult to explain their role in the observed degradation characteristics of these systems. Why the N-alkyl bond in PmDAS should cleave at temperatures associated with the onset of crosslinking is difficult to understand. It is possible that scission of weak structures such as peroxy linkages may either take part in, or catalyze, the removal of the methyl groups by a totally independent process. Peroxy radicals are also known to promote crosslinking of PDAS, PmDAS, and poly(p-N,N-diethylaminostyrene) in air.[14,15]

Degradation of 0.3% solutions of PmDAS in naphthalene for 1 hr, similar to work by Cameron and Grassie[16] on PS, gave a material which was soluble in normal solvents. GPC analysis indicated a small molecular weight decrease. Subsequent pyrolysis of this material gave a residue which was insoluble, suggesting that the crosslinking process was independent of the extent of degradation. In addition, it suggests that weak links formed during polymerization are not responsible for crosslinking and that peroxy groupings which are unlikely to be present after treatment at 250°C are not responsible for the observed crosslinking. Monomer yields obtained from PmDAS showed no dependence on the thermal history of the residue for the higher molecular weight samples and were comparable with the untreated polymer which parallels the behavior previously observed for PDAS.[6]

This suggests that crosslinks formed during the heating cycle can break at higher temperatures or that a low degree of crosslinking fails to inhibit the principal degradation reactions, i.e., unzipping and transfer.

Fraction IV—The Oil

Still and Whitehead[6] found a similar fraction on pyrolysis of PDAS, which was subjected to IR and MS analysis and shown to consist of substituted dimers and trimers similar to those found by Madorsky for PS.[17] In addition, dimeric and trimeric species containing secondary amino groupings were identified.

GPC analysis of the PS and PmDAS oil fractions was made using the calibration (Fig. 1). It can be seen that m-DAS does not lie on the straight line passing through the other standards, and it has been assumed that the m-dimethylamino-substituted derivatives of the standards lie on a calibration curve parallel to that shown. The average molecular weights of the peaks observed for PS and PmDAS oil fractions were assessed using these calibration curves and the data obtained are shown in Table III and Figure 1. The number and point of elution of the peaks were found to be independent of the pyrolysis temperature and the molecular weight of the polymer employed. The components found for PS are in accord with previous studies,[18] and results from PmDAS are similar

to those obtained from PDAS[6] and indicate the oligomeric nature of fraction IV.

In view of studies on the liquid fraction reported in part XXI, it was expected that fraction IV from PmDAS would contain oligomeric products showing evidence of N-alkyl and N-aryl scission and methyl radical transfer reactions to chain radicals. IR analysis indicated that this fraction contained secondary amino groupings and vinylic unsaturation. No evidence was found for the presence of primary amino groupings from chemical tests, which is consistent with the data obtained on the liquid fraction by GLC and GLC/MS.[1] This however differs from the situation reported previously for the isomeric PDAS.[6]

NMR analysis gave complex spectra, indicating the presence of mono-N-methyl and N,N-dimethyl groups and aliphatic, vinylic, and aromatic protons.

A detailed comparative qualitative analysis of fraction IV obtained from both PS and PmDAS was made using GLC/MS and studies by MS using a heated probe. For PS, GLC/MS gave two major components, I (m/e 208), II (m/e 312), a minor component III (m/e 196), and six minor components in insufficient quantity to give spectra allowing interpretation. Compounds I, II, and III were assigned the structures below, which agrees with previous work[19]:
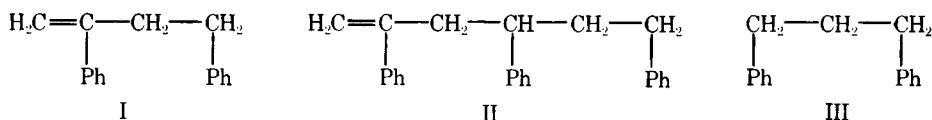

PmDAS gave one component in too small a quantity to allow interpretation of its mass spectrum. The remaining components of fraction IV were too involatile to be eluted from the column.

The mass spectra obtained from PS and PmDAS fraction IV using probe studies contained base peaks at m/e 91 and 134, corresponding to the respective tropylium ions formed by fragmentation of the oligomers:
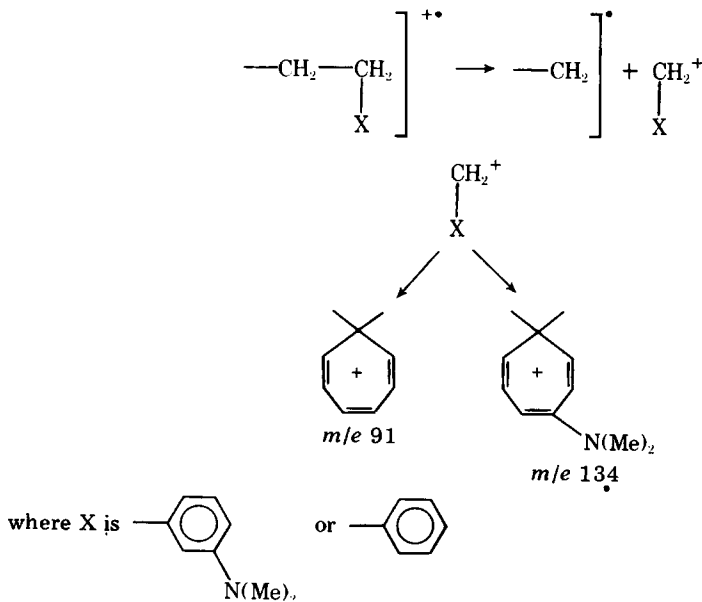
On the basis of these substituted tropylium ions and the molecular ions observed, together with GPC analysis, it was possible to assign structures for components present in fraction IV as shown in Table IV.

In addition to components analogous to products from PS shown in Table IV, an ion at m/e 120 found for PmDAS fraction IV suggests that some oligomers contain secondary amino groupings.   Such an ion is the tropylium ion

m/e 120
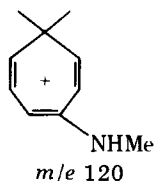
produced by fragmentation of oligomers.   This, together with the IR and NMR evidence on fraction IV and product analysis studies on the liquid fraction,[1] allow the components listed in Table V to be identified.   Such species indicate that N-alkyl scission again occurs.   For the liquid fraction evidence was presented showing that N-aryl scission also occurred and that products resulting from structures produced by combination of chain radicals and methyl radicals were also present.

Evidence is presented in Table VI to suggest that similar reactions occur prior to oligomer formation, resulting in the oligomeric species shown.   N-Aryl cleavage also occurs as exemplified by compounds m/e 251, 253, 265, and 412, where loss of the dimethylamino grouping has occurred and the substituted phenyl radical so produced has combined with a methyl radical formed by N-alkyl scission.   Compounds at m/e 237, 239, and 251 similarly result from loss of the dialkylamino grouping followed by hydrogen abstraction.

Compounds at m/e 296, 308, and 453 are produced by chain radicals combining with methyl radicals to give a system which by loss of hydrogen yields a precursor radical which may yield oligomer by a variety of routes, one of which is shown below:

where X is
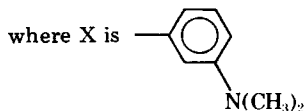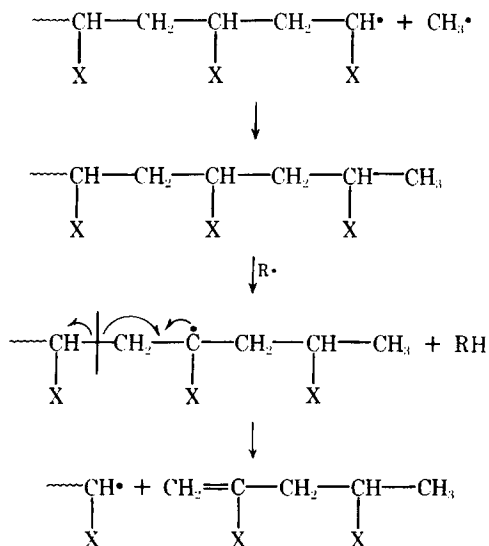
and R· is any radical in the system capable of hydrogen abstraction.

The overall degradation behavior of P*m*DAS is similar to that observed for PS with reactions resulting from N-alkyl and N-aryl bond scission superimposed. Notable differences arise both in the complexity of the products and the insolubility of the residue and the molecular weight dependence of the P*m*DAS system.

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